Current Applied Science and Technology Vol. 23 No. 3 (May-June 2023)

Research article

EIS and Electrical Investigations on (1D) Multiwall Carbon Nanotubes as NAM Additive for Automotive Lead-Acid Battery

Sreedhar Doraswamy[1,2]*, Narendran Dama[1], Suryanarayana Murthy Kurivella[1], Jagadish Mandava[1] and Vasudeva Rao Veeredhi[2]

[1]*Technology Division, Amararaja Batteries Limited, Karakambadi 517520, India*
[2]*Department of Mechanical and Industrial Engineering, University of South Africa, Johannesburg 1710, South Africa*

Received: 3 March 2022, Revised: 22 June 2022, Accepted: 14 December 2022

DOI: 10.55003/cast.2022.03.23.015

Abstract

Keywords

lead-acid batteries;

automotive;

MWCNTs;

negative electrode;

EIS;

charge acceptance;

cranking and cycling ability

Currently, an application like Start-Light-Ignition (SLI) for the automotive industry prefers flooded type lead-acid energy storage and is also vastly adopted energy storage. Lead-acid cells in a battery comprise negative and positive electrodes, separated by an insulating material with industrial-grade H_2SO_4 as an electrolyte. The objective of the present investigation is to overcome the progressive sulphation in the negative electrode and improve the battery's electrical performance. With one dimensional (1D) carbon nano tubes (CNTs) as an additive in the negative electrode of an automotive flooded lead-acid battery (LAB), we try to improve the battery performance. In this study, negative electrodes of LAB were prepared by loading traditional constituents like lead oxide, H_2SO_4, H_2O, polyester binder, lignosulphonate, and Blanc Fixe while limiting MWCNTs to 0.2%. The performance studies of the prepared batteries were conducted, as per Japanese Industrial Standards (JIS). Both the batteries prepared with and without MWCNTs as an additive in negative active materials (NAM) were subjected to electrical assessments to understand the cold cranking ability, cycling stability, and charge acceptance. The batteries were also analyzed by electrochemical impedance spectroscopy (EIS) where the lower charge transfer resistance was observed with the battery having MWCNTs when compared to the control (without MWCNTs) battery. The present investigations established that the MWCNT material, as an additive, played a vital role in laying an improved conductive network across the negative electrodes for higher cycling applications (ISS/Hybrid/EV).

---

*Corresponding author: Tel.: (+91) 9176603143
E-mail: snd@amararaja.com

1. Introduction

In lead-acid batteries, one of the failures is the growth of lead sulfates over a period in the negative plate. This development of lead sulfates is termed as ‘sulphation’. Once these lead sulfates ($PbSO_4$) become significant and hard to reduce to their original form (Pb), then they impact the performance of the batteries [1]. Due to the sulfates, the life of the battery and also short-term requirements like cranking, charge acceptance, etc., also gets reduced significantly. In growing demand in Hybrid/EV applications, the sulfates are proliferated at higher pace in the negative electrode which has an impact on the battery performance [2]. Several researchers have addressed different types of carbon like carbon black, lamp black, furnace black, etc., with varying areas of the surface where the carbons form a conductive path throughout the electrode. However, with these carbons, high hydrogen evolutions (water loss) at negative electrodes were also observed. Over a while, at different depths of discharge (DoD), these conductive paths are overlapped with the growing lead sulfates and make the carbon inaccessible due to the presence of carbon in the amorphous phase [3, 4]. Also, the shape of the added carbons plays a vital role in maintaining the conductive path alive, as the regular carbon is most spherical and tends to lose the connectivity at higher operational conditions [5]. Carbon with different allotropes, especially low dimensional carbons or nano carbons with unique shapes like wire, tube (1D), sheets (2D), etc., are gaining more attention as the sulfate inhibitor. Nano carbons are carbon with high structural stability and have one dimension in the nanoscale (<100nm). As the carbons and their allotropes have different surface areas and pore structures, they tend to change the structure of the electrode when added and therefore alter the electrode/plate’s surface area [6, 7]. All the changes in the structure surface area of the electrodes depend on the atomic arrangements of the carbon. Like the sizes of carbon, particles do impact the performance of the batteries, but only at initial discharges. However, the cranking ability required for igniting the engines could not help [8]. Having the 1D carbon (carbon nanotubes) with a higher concentration (>0.2%) could lead to higher hydrogen evolution even though it increases the capacitance of the electrode. If the loading of CNTs is optimized with ≤0.2%, the hydrogen evolution will be in control and help the batteries to perform better [9]. As discussed, the initial capacity of the batteries can be improved with the high surface area carbons, which is attributed to the energy density. The cranking ability and the charge acceptance behavior are critical parameters in defining the Hybrid/EV application requirements. Improving these parameters is challenging and can be achieved with low dimensional carbons or nano carbons [10, 11]. Another critical parameter for advance requirements is the cycling ability of the battery at high-rate partial state of charge (HRPSoC) condition. So far, the works published on MWCNTs for lead acid energy storage and the test protocols were with 2V system. Now it has become very much essential to know the importance of the parameters like dynamic charge acceptance, deep cycling and high current discharges, for 12V system [12, 13]. In this work, we presented the batteries (12V) made with MWCNTs and studied the performances with the commercially available carbon black batteries. Embedding highly structured MWCNTs in the negative active material could help gain more cycle life under this condition. The structure of MWCNTs is wire type and spreads the conductive path uniformly across the electrode. Due to the porous structure of the CNTs, the electrolyte is easily accessed and behaves like a reservoir. The higher charge transfers with lower resistance could perform better with lower water losses [14, 15]. All the electrical tests like discharge capacity, cranking ability, charge acceptance test, HRPSoC (charging/discharging) cycles, and water loss (hydrogen evolution) tests are carried out under Japanese Industrial Standard (JIS - 5301- 2006). The mechanism of MWCNTs as an additive in the negative electrode was explored in this work and presented as a potential candidate in enhancing the performance of the batteries in a futuristic way.

2. Materials and Methods

The Carbon Black (CB) and Multiwall Carbon Nanotubes (MWCNTs) were commercially procured from Philips carbon and Sigma Aldrich with purity of 99% and 98%, respectively. The particle size of Carbon Black used was 3 microns (D50), the outer diameter of the MWCNT was 10 nm and the length was 6 microns. Their morphological study was carried out with scanning electron microscopy (SEM-JEOL, JSM-6010 Plus/LV, Japan). In Figure 1, SEM images of Carbon Black and MWCNTs reveals that the Carbon Black material comprises of numerous particles, whereas a wire type distribution is observed for MWCNTs.

The XRD spectra of both CB and MWCNTs are shown in Figure 2. The diffraction studies were carried out by X-ray diffraction spectroscopy supplied by Rigaku, Japan. The XRD pattern of MWCNTs shows the high-intensity peak at 2θ = 25.897° and CB gave a rise at 2θ = 24.749° corresponding to the (002) reflection. At 44.335° from MWCNTs XRD pattern, a 2nd peak was observed due to the catalyst used for CNT synthesis, compared with ICDD - DB card numbers: 04-018-7559; 01-074-5561 (NiC). The presence of carbonaceous material in the CB was observed from the XRD pattern and compared with ICDD - DB card numbers: 04-015-0267.

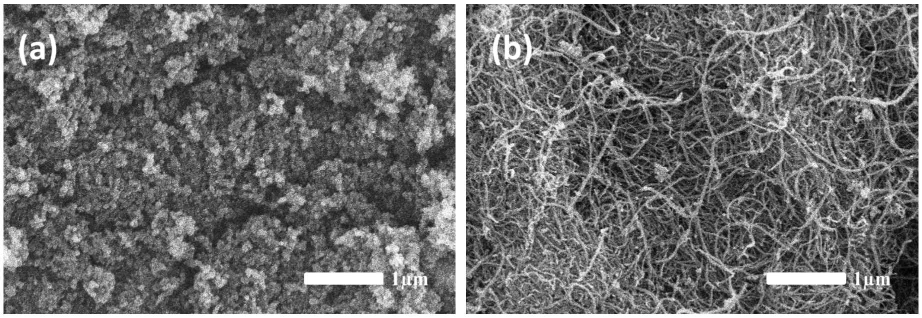

Figure 1. SEM images of (a) Carbon Black (b) MWCNTs

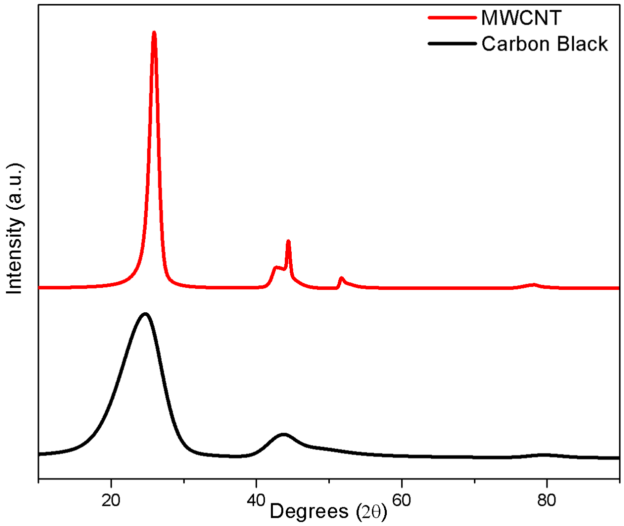

Figure 2. XRD spectra of Carbon Black and MWNCT's

The materials involved in building 12Volts-65Ampere-Hour (Ah) rated batteries were similar with the positive electrodes. In addition, the change was only with the negative electrode's additives, the Carbon Black in the control batteries, and MWCNTs in trial batteries. They were restricted to 0.2% loading to the lead grids. Other additives like lignosulphonate, Blanc Fixe ($BaSO_4$), binder (polyester fibers), and sulfuric acid (H_2SO_4) were added in the negative electrode preparation. The prepared electrodes/plates were further cured at 60±2°C in a curing chamber for two days to obtain 3BS (tribasic lead sulfates). With six negative and five positive plate electrodes the 65Ah rated battery was designed and these electrodes were assembled with a polyethylene (PE) separator as shown in Figure 3. The cells were filled with diluted sulfuric acid (H_2SO_4) electrolyte with a specific gravity of 1.245. The prepared batteries were electrically tested as per JIS protocol by Bitrode Instruments, USA.

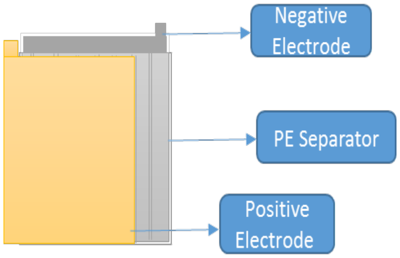

Figure 3. Schematic representation of LAB cell

3. Results and Discussion

3.1 Impedance spectroscopy

EIS was performed, and Nyquist plots were developed by two electrode mode with control and MWCNT batteries having 100% state of charge (SoC). The EIS test was carried out with the amplitude of 10mV and the frequency ranging from 1KHz to 0.1Hz. In Figure 4, it was noticed from the Nyquist plot that the control battery curve is marginally ahead at high frequency compared to the MWCNTs plot. This is because the surface resistance of the Control electrode is low compared to that of MWCNT. But the charge transfer resistance (R_1) is higher in the control battery than in MWCNT batteries. This means that the conductivity of the MWCNTs is high and dispersed uniformly. The illustration from Figure 4 is the nonlinear least-square fitted program, and associated parameters refer to the electrode behavior with the EIS instrument supplied by Wonatech, Korea. The electrode-electrolyte interference resistance (Rs), charge transfer resistances (R_1), diffusion resistance (R_2) which are associated to the porosity of the electrodes, and capacitance from the behavior of constant phase element (Q_1) and ideal capacitor (C_2) were obtained and tabulated in Table 1. From the EEC, the inductance (L_s) is attributed to the terminal connections of the inside cell. The equivalent electrical circuit (EEC) with the best fit was also obtained and shown in Figure 5. These results suggest that the addition of MWCNTs significantly reduces the charge transfer resistances developed from the reaction with the electrolyte and electrode, promoting the redox reaction more effectively. The capacitance (C_2) represents the ions' diffusion process (H^+ and SO^-_4) on the electrode surface. Another type of capacitance, is a constant phase element (Q) due to the rough surface of the electrodes, having the phase (n) 0.8 for control and 0.7 for MWCNT. The higher capacitance value with the MWCNTs is attributed to the thickness of the reaction layer formed with the ions [16].

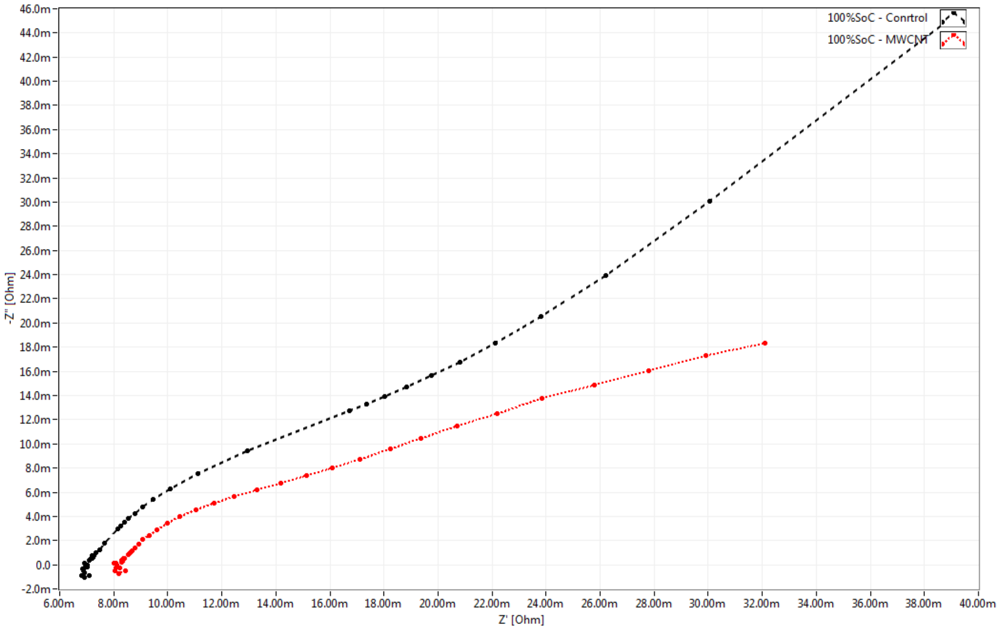

Figure 4. Nyquist plot of 100% SoC - 12V lead acid control (Black Line); MWCNT (Red Line)

Table 1. EIS parameters of control and MWCNT 12V battery with 100% SoC

Parameters	Control	MWCNT
L_s	0.121 x 10^{-6}	0.141 x 10^{-6}
R_s (mΩ)	7.11	8.09
Q_1 (S·s^n)	10.72	15.57
R_1 (Ω)	0.21	0.06
C_2 (F)	13.31	16.34
R_2 (Ω)	0.051	0.044

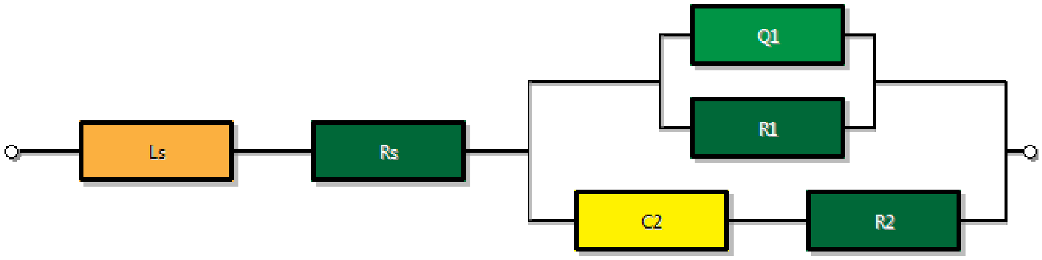

Figure 5. Equivalent Electrical Circuit (EEC) for 12V LAB system

3.2 Electrical performance

Performance of batteries with high discharging rate frequently address the issue for engine cranking application in the automotive industry. Here, the MWCNT battery shows an optimistic effect on the duration w.r.t discharging capabilities. Figure 6(a) shows a 25% increase of MWCNTs negative plates in taking the time to reach 6V @300A conditioned at -18ºC. The charge acceptance was measured at the 10th min by applying a constant voltage of 14.4V. The observations from Figure 6(b) confirm that adding MWCNTs has improved charge acceptance by 15%, compared to CB. This is due to an enhanced conductive network across the plates promoting the transport of H^+ and SO^-_4 ions and enhancing the utilization rate of the active mass. The discharge capacity at 5 h rate (C_5 Hr) was performed, where the current rating 13Amps was applied to the battery's nominal capacity and calculated to reach >80% of the designed capacity (65Ah). From Figure 6(c), the experimental results show that the discharge capacity of batteries containing MWCNTs was better (8%) than the CB batteries. This suggests that MWCNTs provide a uniform conductive network in the electrode and restrict the sulphation process with higher active material utilization [6].

Water loss, which is the measurement of the amount of battery electrolyte decreased by overcharging subjected to 14.45V at 40±2°C, is another critical aspect that directly impacts the battery electrolyte. Under overcharging duty, the H_2 recombination efficiency is a life-limiting mechanism. Significant gassing occurs during each recharge cycle [17]. From Figure 6(d), it is evident that the MWCNTs negative plate has a consistent behavior for an extended period whereas the CB batteries have considerable fluctuations in voltage, leaving higher gassing than MWCNTs containing batteries. The water loss in MWCNTs batteries and CB batteries is 0.4g/Ah and 0.7g/Ah, respectively. Accordingly, the water loss in the MWCNT battery is about 42% less than in the control battery.

High-rate charging/discharging operations were carried out by limiting SoC to 50% of 5Hr rate capacity. The effect of MWCNT on the batteries' life cycle under standard operating conditions is shown in Figure 7(a) and (b). As a result, the cycling life of the CB battery was less than 125 cycles. The cyclic life of the MWCNTs battery could be extended to 175 cycles under the same conditions, which is 40% higher than the control battery. Therefore, the addition of nanomaterials like MWCNTs in the negative electrodes promotes electron transfer and accelerates the charging process which benefits the charge/discharge cycling process. Hence, using carbon nanomaterials in the active material retards the growth and deactivation of $PbSO_4$ to improve the utilization of active material in deep discharge applications [18]. According to the surface morphology from Figure 8 (a) and (b), it is evident that the CB negative electrodes consisted of large $PbSO_4$ particles and the negative plate with MWCNTs has small $PbSO_4$ particles, which are easy to reduce even after 125 charging/discharging cycles. That is why the MWCNTs battery could deliver higher cycles than the CB battery.

Thus, MWCNTs was proved to limit the formation of sulfation at negative plates and further increased the batteries' cycling (50 cycles) capability. Therefore, MWCNTs could become prime additive material in negative electrode for flooded lead acid batteries.

4. Conclusions

From the studies, the addition of MWCNTs as a NAM additive experienced a lower charge transfer resistance with increased capacitance. It also enhanced the performance of the batteries at higher current rate cycling and restricts water evaporation. It is also concluded that by adding MWCNTs, the charge acceptance has improved by 15% and 40% enhancement of HRPSoC cycles. With

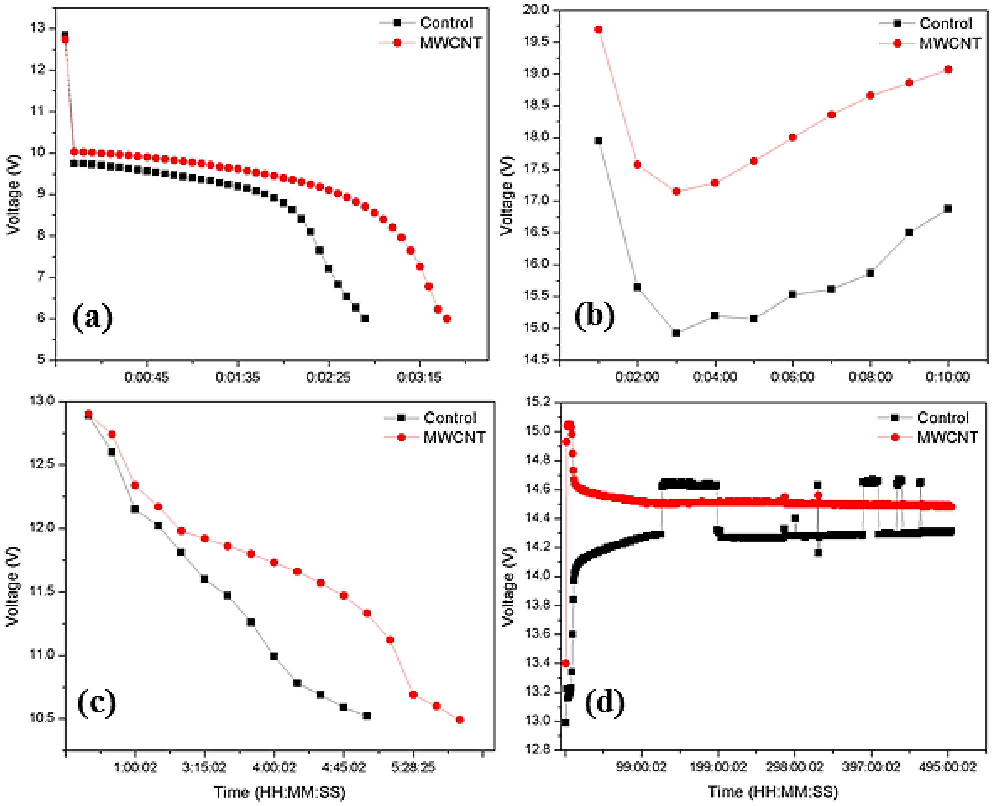

Figure 6. Electrical testing of CB (control) and MWCNTs electrodes (a) Cranking ability (b) Charge acceptance (c) Discharge capacity (d) Over charging potential

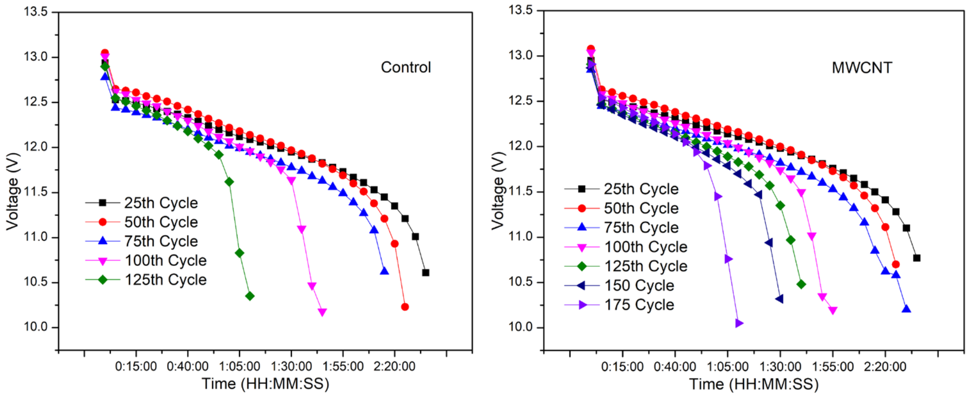

Figure 7. Charge/Discharge cycling (HRPSoC) of CB (control) and MWCNTs electrodes

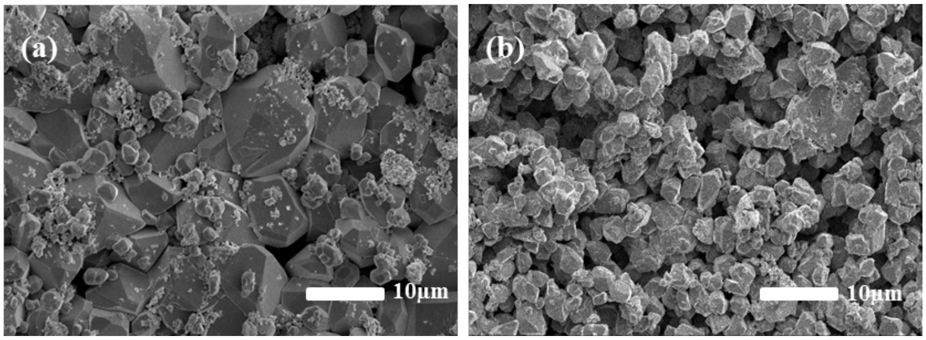

Figure 8. SEM images of (a) CB – control (b) MWCNTs negative plates after 125 cycles

MWCNTs, an 8% enhancement in initial discharge capacity and 25% improvement in cranking ability of batteries was achieved. Due to the 1D/tube type structure, the conductive network has effectively leveraged active material utilization. Thus, with the results obtained, the MWCNTs could be considered one of the effective nano carbons for constructing the LAB's negative electrodes and could be explored for 100% DoD application due to its lower water loss.

5. Acknowledgements

The authors would like to thank the management and the staff of Amararaja Batteries Limited, India, and The University of South Africa (UNISA) for this work's assistance and support.

References

[1] Nakamura, K., Shiomi, M., Takahashi, K. and Tsubota, M., 1996. Failure modes of valve-regulated lead/acid batteries. *Journal of Power Sources*, 59, 153-157, DOI: 10.1016/0378-7753(95)02317-8.

[2] Shiomi, M., Funato, T., Nakamura, K., Takahashi, K. and Tsubota, M., 1997. Effects of carbon in negative plates on cycle-life performance of valve-regulated lead/acid batteries. *Journal of Power Sources*, 64, 147-152, DOI: 10.1016/S0378-7753(96)02515-3.

[3] EUROBAT, 2013. *A Review of Battery Technologies in Automotive Applications – Full Report*. [online] Available at: https://www.eurobat.org/wp-content/uploads/2021/09/rev_of_battery_ executive _web_1.pdf.

[4] Sauer, D.U., 2009. Secondary batteries – lead– acid systems | lifetime determining processes. *Encyclopedia of Electrochemical Power Sources*, 805-815, DOI: 10.1016/B978-044452745-5.00137-4.

[5] Wang, J., Hou, H., Hu, J., Wu, X., Hu, Y., Li, M., Yu, W., Zhang, P., Liang, S., Xiao, K., Kumar, R.V. and Yang, J., 2019. Mechano-chemical synthesis of high-stable PbO@C composite for enhanced performance of lead-carbon battery. *Electrochimica Acta*, 299, 682-691, DOI: 10.1016/j.electacta.2019.01.063.

[6] Pavlov, D., Nikolov, P. and Rogachev, T., 2011. Influence of carbons on the structure of the negative active material of lead-acid batteries and on battery performance. *Journal of Power Sources*, 196, 5155-1567, DOI: 10.1016/j.jpowsour.2011.02.014.

[7] Doraswamy, S.N., Srinivas, K., Murthy, K.S.N., Jagadish, M. and Vasudeva R., 2021. Effect of milled carbon as negative electrode additive for lead acid energy storage device. *Materials Today: Proceedings*, 38(5), 3131-3135, DOI: 10.1016/j.matpr.2020.09.501.

[8] Frackowiak, E. and Béguin, F., 2002. Electrochemical storage of energy in carbon nanotubes and nanostructured carbons. *Carbon*, 40, 1775-1787, DOI: 10.1016/S0008-6223(02)00045-3.

[9] Prosini, P.P., Pozio, A., Botti, S. and Ciardi, R., 2003. Electrochemical studies of hydrogen evolution, storage and oxidation on carbon nanotube electrodes. *Journal of Power Sources*, 118, 265-269, DOI: 10.1016/S0378-7753(03)00097-1.

[10] Moseley, P.T., 2009. Consequences of including carbon in the negative plates of valve-regulated lead–acid batteries exposed to high-rate partial-state-of-charge operation. *Journal of Power Sources*, 191, 134-138, DOI: 10.1016/j.jpowsour.2008.08.084.

[11] Simon, P. and Burke, A., 2008. Nanostructured carbons: double-layer capacitance and more. *The Electrochemical Society Interface*, 17(1), 38-43.

[12] Saravanan, M., Sennu, P., Ganesan, M. and Ambalavanan, S., 2013. Multi-walled carbon nanotubes percolation network enhanced the performance of negative electrode for lead-acid battery. *Journal of Electrochemical Society*, 160(1), DOI: 10.1149/2.062301jes.

[13] Banerjee., A., Ziv, A., Shilina Y.A., Levi, E., Luski, S. and Aurbach, D., 2017. Single-wall carbon nanotube doping in lead-acid batteries: A new horizon. *ACS Applied Materials and Interfaces*, 9 (4), 3634-3643, DOI: 10.1021/acsami.6b13377.

[14] Simon, P. and Gogotsi, Y., 2013. Capacitive energy storage in nanostructured carbon–electrolyte systems. *Accounts of Chemical Research*, 46, 1094-1098, DOI: 10.1021/ar200306b.

[15] Povlov, D. and Nikolov, P., 2013. Capacitive carbon and electrochemical lead electrode systems at the negative plates of lead-acid batteries and elementary processes on cycling. *Journal of Power Sources*, 242, 380-399, DOI: 10.1016/j.jpowsour.2013.05.065.

[16] Pavlov, D. and Petkova, G., 2002. Phenomena that limit the capacity of the positive lead acid battery plates. *Journal of Electrochemical Society*, 149(5), A654-A661, DOI: 10.1149/1.1468645.

[17] Zou, X., Kang, Z., Shu, D., Liao, Y., Gong, Y., He, C., Hao, J. and Zhong, Y., 2015. Effects of carbon additives on the performance of negative electrode of lead-carbon battery. *Electrochimica Acta*, 151, 89-98, DOI: 10.1016/j.electacta.2014.11.027.

[18] Hu, H-Y., Xie, N., Wang, C., Wang, L-Y., Privette, M.P., Li, H-F., Pan, M., Wu, F., Yan, X-L., Jiang, B-B., Wu, M.H., Vinodgopal, K. and Dai, G-P., 2018. Enhanced performance of E-bike motive power lead–acid batteries with graphene as an additive to the active mass. *Omega*, 3(6), 7096-7105, DOI: 10.1021/acsomega.8b00353.